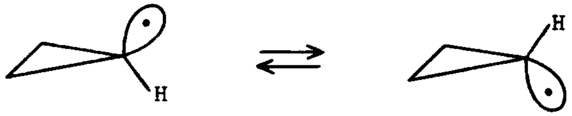
Tetrahedron Letters No. 25, pp. 2247-2250, 1971. Pergamon Press. Printed in Great Britain.

NITROGEN-CENTERED FREE RADICALS. II. ESR SPECTRA OF THE AZIRIDINO AND AZETIDINO RADICALS IN SOLUTION [1,2]

Wayne C. Danen and Terry T. Kensler
Department of Chemistry, Kansas State University
Manhattan, Kansas 66502

(Received in USA 12 May 1971; received in UK for publication 18 May 1971)

There is currently much interest in the electronic properties of strained rings with the aziridine and azetidine ring systems receiving considerable attention because of the relatively high barrier to inversion about nitrogen (3). Electron spin resonance (esr) spectroscopy is ideally suited to the study of paramagnetic species in that it not only "maps" the location of the unpaired electron but also yields detailed information concerning the type(s) of orbital in which the electron resides. Although most alkyl and cycloalkyl radicals are planar pi radicals, the classical esr study of Fessenden and Schuler (4) has demonstrated that the cyclopropyl radical is a notable exception. The abnormal α hyperfine coupling constant of 6.5 G and the fact that the four β hydrogens appear equivalent with a splitting of 23.42 G is interpreted in terms of a rapidly inverting sigma radical.



In our earlier work with the dialkylamino radicals (1) we had shown that these species are pi radicals with the unpaired electron localized primarily in a _p_ orbital on nitrogen. We presently wish to report the high-resolution esr spectrum of the aziridino radical which, by analogy to the isoelectronic cyclopropyl radical, might be expected to exist as a sigma radical _1_ with the unpaired electron residing in a hybrid orbital with appreciable _s_ character. After unsuccessful attempts to prepare the tetrazene precursor to the aziridino radical (1) we found

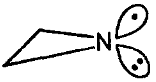
Figure 1. ESR spectrum of the aziridino radical in cyclopropane solution at -100° C.

Table 1

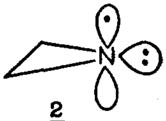
Radical	a^N	a^H_β	g-value
Aziridino	12.52	30.70	2.0043 ± 0.0001
Azetidino	13.99	38.25	2.0045 ± 0.0001

Both spectra in cyclopropane solution at -100° C. Hyperfine splitting constants and g-values relative to Fremy's salt taken as 13.091 G and 2.0055, respectively (R. J. Faber and G. K. Fraenkel, J. Chem. Phys., 47, 2462 (1967); J. Q. Adams and J. R. Thomas, ibid., 39, 1904 (1964)). The g-values are corrected for second-order effects.

that irradiation of a solution of aziridine and di-t-butylperoxide in cyclopropane at reduced temperatures (6) produces a well-resolved spectrum of the aziridino radical (Figure 1). The



1

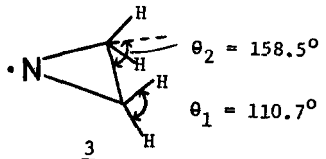


2

spectrum is readily analyzed in terms of a nitrogen splitting of 12.52 G and four equivalent hydrogens of 30.70 G. The g-value of 2.0043 ± 0.0001 is within experimental error of that for dimethylamino radical generated from tetramethyltetrazene (2.0044 ± 0.0001) and rules out the present spectrum as resulting from a nitroxide radical which would exhibit a g-value of ca. 2.0060. The presently observed hydrogen splitting and g-value are in good agreement with those reported for this radical produced by γ-irradation in the solid state (7).

The 12.52 G isotropic nitrogen hyperfine interaction is quite similar to that observed for the simple dialkylamino radicals (1) and indicates that the aziridino radical is likewise a pi radical with the unpaired electron located primarily in the nitrogen 2p orbital (cf. 2). The heavily p-weighted C-N and C-C bonds in the aziridino radical are apparently balanced by a high s character primarily in the lone pair of electrons rather than in the orbital containing the unpaired electron as in the cyclopropyl radical.

The above conclusions are supported by INDO calculations. A complete INDO energy minimization (8) yields the following structure for the aziridino radical in which C-N = 1.43 Å, C-C = 1.46 Å, C-H = 1.12 Å, θ_1 = HCH angle, and θ_2 = the angle formed by the HCH bisector and the C-C bond. The calculations predict a^N = 10.25 G and a^H = 29.84 G in good agreement with experiment



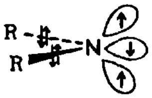
3

and indicate that there is a spin density of 0.8895 in the nitrogen _2p_ orbital and only 0.0270 in the nitrogen _2s_ orbital.

The esr spectrum of the four-membered ring azetidino radical is qualitatively similar to that of the aziridino and readily analyzed to give the hyperfine coupling constants and g-value reported in Table 1. The β-hydrogen splittings of 38.25 G may be compared to that reported for the β hydrogens of the cyclobutyl radical, 36.77 G (10). Partially resolved second-order splittings of the central lines of the spectrum were observed but the resolution was not sufficient to unambiguously assign a coupling constant to the γ hydrogens; it appears that this interaction must be of the order of 0.5 G or less.

It has been argued that there should be a strong dependence of a^N and g-value on the CNC bond angle in neutral amino free radicals (11). The rather similar nitrogen coupling constants and almost identical g-values for the aziridino and azetidino radicals (with CNC internuclear angles of _ca_. 60° and 90°, respectively) as compared to the open chain dimethylamino radical (with CNC angle _ca_. 117° (11,12)) would appear to preclude a reliable estimate of the CNC internuclear angle in dialkylamino radicals on the basis of these parameters.

Although a single canonical structure such as 2 illustrates that there is but a small spin density in the nitrogen _2s_ orbital, an alternate but equivalent description of amino radicals can be made in terms of localized molecular orbitals (13). Qualitatively, such a description yields 4 as the electronic structure for a neutral dialkylamino radical and emphasizes that the alpha



4

(↑) and beta (↓) electrons occupy different orbitals. Although perhaps not immediately obvious from a description similar to 4, it is important to realize that the nitrogen 2s orbital spin density (i.e., the difference between the alpha and beta electron densities in the nitrogen 2s orbital) in, e.g., the aziridino radical is not changed from that given above. The concept of localized molecular orbitals as applied to amino radicals will be discussed in detail elsewhere (12).

REFERENCES

1. Part I. W. C. Danen and T. T. Kensler, J. Amer. Chem. Soc., 92, 5235 (1970).

2. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF No. 5579-AC4) and the Kansas State University Bureau of General Research for support of this work.

3. H. Kessler, Angew. Chem. Int. Ed. Engl., 9, 219 (1970).

4. R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39, 2147 (1963).

5. A PEK A-1-B, 2000 watt, high pressure mercury capillary lamp was utilized in conjunction with a spherical reflecting mirror and a suitable lens system.

6. P. J. Krusic and J. K. Kochi, J. Amer. Chem. Soc., 90, 7155 (1968).

7. D. Cordischi and R. Di Blasi, Can. J. Chem., 47, 2601 (1969), report a^H = 30.0 G and g = 2.0044 ± 0.0004; V. I. Trofimov and I. I. Chkheidze, Khim. Vys. Energ., 1, 324 (1967) (Chem. Abstr., 68, 12244z (1968)), give a^H = 29 G. Neither of these groups of workers was able to obtain the nitrogen hyperfine coupling constant because of anisotropic broadening effects.

8. The minimum energy structure 3 was determined by starting with the structure of aziridine (9) and systematically varying the C-N, C-C, C-H, θ_1 (HCH angles), and θ_2 (angle between HCH plane and C-C bond) in that order.

9. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, Special Publication No. 11, M 134, 1958.

10. J. K. Kochi, P. J. Krusic, and D. R. Eaton, J. Amer. Chem. Soc., 91, 1877 (1969).

11. D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, Abstracts, Second Symposium on Electron Spin Resonance, Athens, Ga., Dec., 1970, D5.

12. W. C. Danen, T. T. Kensler, and K. F. Purcell, unpublished results.

13. D. M. Hirst and M. E. Linington, Theoret. chim. Acta (Berl.), 16, 55 (1970); C. Edmiston and K. Ruedenberg, Rev. Mod. Phys., 35, 457 (1963).